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Mapping local shape dependent electromagnetic field enhancements in single metallic nanoparticles using stochastic optical reconstruction microscopy (STORM)

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Final Report

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14. ABSTRACT

The goal of this project was to use novel approaches in super-resolution optical imaging to probe local electromagnetic field enhancements in plasmonic metal nanoparticles. To that end, we have made several important contributions to this goal through the support provided by AFOSR. First, we were the first group to use super-resolution optical imaging to map out the local electromagnetic field intensity of a single-molecule surface enhanced Raman scattering (SM-SERS) hot spot with <1 nm resolution. Second, we were the first to provide a correlation between the size and shape of SM-SERS hot spots and the structure of the underlying nanoparticle. Third, we demonstrated a unique, rapid, all-optical readout for the output polarization of SM-SERS nanoparticles and showed that SERS-active nanoparticle dimers could be discriminated from higher order aggregates without the need for separate structure characterization tools. These accomplishments represent significant forward progress in our understanding of SM-SERS hot spots, which are well-known to be the sites with the strongest electromagnetic enhancement, yet remain quite difficult to fabricate in a rational manner.

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Final report: Mapping local shape dependent electromagnetic field enhancements in single metallic nanoparticles using stochastic optical reconstruction microscopy (STORM)

Program: Molecular Dynamics
Program Manager: Dr. Michael R. Berman

PI: Katherine A. Willets, Department of Chemistry and Biochemistry, University of Texas at Austin

Project summary: The goal of this project was to use novel approaches in super-resolution optical imaging to probe local electromagnetic field enhancements in plasmonic metal nanoparticles. To that end, we have made several important contributions to this goal through the support provided by AFOSR. First, we were the first group to use super-resolution optical imaging to map out the local electromagnetic field intensity of a single-molecule surface enhanced Raman scattering (SM-SERS) hot spot with <1 nm resolution. Second, we were the first to provide a correlation between the size and shape of SM-SERS hot spots and the structure of the underlying nanoparticle. Third, we demonstrated a unique, rapid, all-optical readout for the output polarization of SM-SERS nanoparticles and showed that SERS-active nanoparticle dimers could be discriminated from higher order aggregates without the need for separate structure characterization tools. These accomplishments represent significant forward progress in our understanding of SM-SERS hot spots, which are well-known to be the sites with the strongest electromagnetic enhancement, yet remain quite difficult to fabricate in a rational manner.

Accomplishment 1: Super-resolution optical imaging to map out the local electromagnetic field intensity of a single-molecule surface enhanced Raman scattering (SM-SERS) hot spot with <1 nm resolution

1) S.M. Stranahan and K.A. Willets. "Super-resolution Optical Imaging of Single-Molecule SERS Hot Spots," *Nano Letters* 10, 3777-3784 (2010). (Featured in C&E News, August 30, 2010)

2) K.A. Willets, S.M. Stranahan, M.L. Weber. "Shedding light on surface-enhanced Raman scattering hot spots through single molecule super-resolution imaging." *J. Phys. Chem. Lett.* 3, 1286-1294 (2012). Journal cover art.

We demonstrated the ability to measure the spatial origin of SM-SERS signals by using point spread function fitting. Briefly, the diffraction limited spot of a single molecule emitter was fit to a 2-D Gaussian function, and the emission centroid was recorded. Next the average intensity as a function of centroid position was plotted for a time series of data to create a map of the SM-SERS hot spot. Figure 1 shows examples of a typical SM-SERS hot mapped using this method. Several important conclusions emerge from these data: (1) the SERS

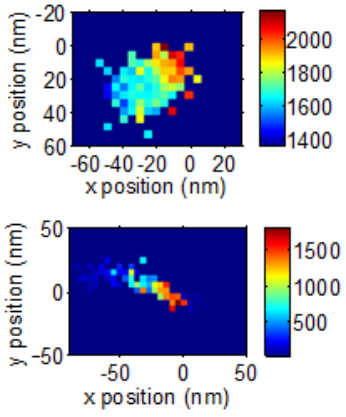

Figure 1. SERS hot spot maps showing how SM-SERS intensity (color bar) varies with the spatial origin of the signal. From ref. 1.

intensity changes in a directional, gradient fashion as the SERS centroid shifts away from the "hottest" spot and (2) the SERS hot spot extends over a region much larger than the size of a single molecule. These data represent the first images of a SM-SERS active hot spot, as reported by a single molecule emitter within that hot spot.

Accomplishment 2: Correlating the size and shape of SM-SERS hot spots with the structure of the underlying nanoparticle

3) M.L. Weber, K.A. Willets. "Correlated super-resolution optical and structural studies of surface-enhanced Raman scattering hot spots in silver colloid aggregates." *J. Phys. Chem. Lett.* 2, 1766-1770 (2011). (Featured in *ACS Noteworthy Chemistry*, August 1, 2011)

4) M.L. Weber, J.P. Litz, D.J. Masiello, K.A. Willets. "Super-resolution imaging reveals a difference between SERS and luminescence centroids." *ACS Nano. 6*, 1839-1848 (2012). (Highlighted in "In Nano," *ACS Nano*. 6, 990-992 (2012)).

To understand how the SERS spatial intensity maps are related to nanoparticle structure, we performed correlated optical and electron microscopy.[3,4] Figure 2, A and B, shows two examples in which the SERS hot spot maps determined from super-resolution imaging are overlaid on the corresponding SERS-active nanoparticle structure.[3] As above, we observe a region of high intensity, accompanied by a directional and gradient decay in the SERS intensity. In both examples, the orientation of the high intensity edge matches the alignment of a junction within the nanostructure, and the gradient decay in the SERS intensity agrees with expectations that the EM field enhancement decreases further from the junction. Thus, we find excellent qualitative agreement between the shape of the spatial intensity maps and the expected local EM enhancement of the nanoparticles.

We also exploited the inherent luminescence signal from silver nanoparticles to substantiate our assignment of the "hot" junction.[4] Figure 2C shows a SERS-active trimer with its corresponding SERS hot spot map overlaid on the rightmost junction. A white "x" marks the position of the nanoparticle luminescence relative to the SERS signal. Discrete dipole approximation calculations of the predicted luminescence and SERS centroids are shown in Figure 2D (in collaboration with David Masiello at the University of Washington) and show excellent agreement with our experimental assignments.[4] These data demonstrate that the shape and intensity distribution of the hot spot track with the local distribution of plasmonic enhancement on the nanoparticle aggregate.

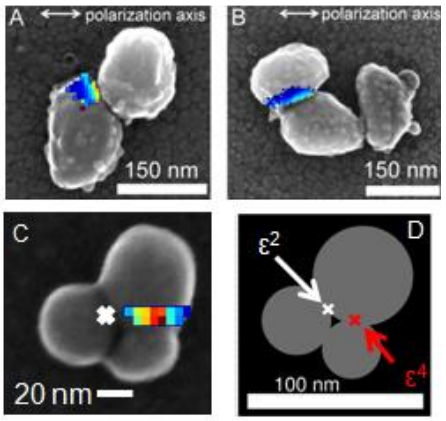

Figure 2. (A-B) SERS hot spot maps overlaid on the corresponding SERS-active nanoparticle structures. From ref. 3. (C) Same as A-B but with the silver luminescence centroid included (white x). (D) Calculated average centroid positions for luminescence (white x) and SERS (red x). From ref. 4.

Accomplishment 3: a unique, rapid, all-optical readout for the output polarization of SM-SERS nanoparticles

4) S.M. Stranahan, E.J. Titus, K.A. Willets. "SERS orientational imaging of silver nanoparticle dimers." *J. Phys. Chem. Lett.* 2, 2711–2715 (2011).

5) S.M. Stranahan, E.J. Titus, K.A. Willets. "Discriminating nanoparticle dimers from higher order aggregates through wavelength-dependent SERS orientational imaging." *ACS Nano.* 6, 1806-1813 (2012).

Because junctions between adjacent nanoparticles are so critical for optimal SERS enhancement, a number of researchers have devised methods for self-assembly of dimers and higher-order aggregates. However, to confirm the resulting aggregation state, structural characterization methods like electron microscopy or atomic force microscopy (AFM) are required, which are time consuming and potentially perturbative. We have developed a simple, rapid (<2 seconds), all-optical method for determining the orientation and aggregation state of nanoparticles, by imaging the SERS signal from adsorbed tags.[4,5]

It is well-known that a single emitting dipole will have a characteristic emission pattern in the far-field, which can be imaged by defocusing the signal onto a two-dimensional detector. We employed a similar approach for studying SERS-active nanoparticle dimers and found that the resulting image reflected the orientation of the underlying dimer, as shown in Figure 3, A-C.[4] By modeling the dimer as a dipole based on its geometry, we found excellent agreement between predicted emission patterns and the three-dimensional dimer orientation.

We also showed that using two different excitation wavelengths allowed us to discriminate dimers from higher order aggregates.[5] In the case of a nanoparticle dimer, the emission patterns are wavelength independent (Figure 3, A-C), while in trimers (and higher order aggregates), the pattern strongly depends on excitation wavelength (Figure 3, D-I). This approach allows for rapid identification of aggregated nanostructures in complex and dynamic environments where AFM and electron microscopy may be less useful.

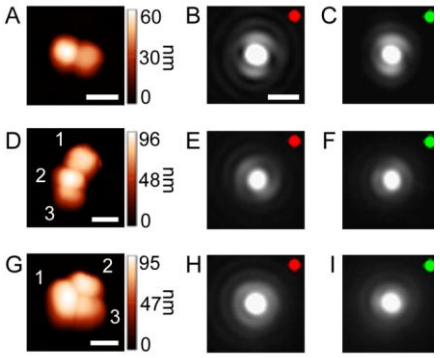

Figure 3. (A) AFM image and corresponding emission patterns with (B) 642 nm and (C) 532 nm excitation for a SERS-active nanoparticle dimer. (D-F) and (G-I) Same as (A-C) but with nanoparticle trimers. From ref. 4.

<u>Additional work citing AFOSR support:</u>

K.A. Willets. "Probing local electromagnetic field enhancements on the surface of plasmonic nanoparticles." *Prog. Surf. Sci.* 2012, accepted.

K.A. Koen, M.L. Weber, K.M. Mayer, E. Fernandez, K.A. Willets. "Spectrally-resolved polarization anisotropy of single plasmonic nanoparticles excited by total internal reflection." *J. Phys. Chem. C.* 116, 16198−16206 (2012).

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Katherine A. Willets

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10. Reporting Period End Date

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11. Abstract

The goal of this project was to use novel approaches in super-resolution optical imaging to probe local electromagnetic field enhancements in plasmonic metal nanoparticles. To that end, we have made several important contributions to this goal through the support provided by AFOSR. First, we were the first group to use super-resolution optical imaging to map out the local electromagnetic field intensity of a single-molecule surface enhanced Raman scattering (SM-SERS) hot spot with <1 nm resolution. Second, we were the first to provide a correlation between the size and shape of SM-SERS hot spots and the structure of the underlying nanoparticle. Third, we demonstrated a unique, rapid, all-optical readout for the output polarization of SM-SERS nanoparticles and showed that SERS-active nanoparticle dimers could be discriminated from higher order aggregates without the need for separate structure characterization tools. These accomplishments represent significant forward progress in our understanding of SM-SERS hot spots, which are well-known to be the sites with the strongest electromagnetic enhancement, yet remain quite difficult to fabricate in a rational manner.

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